Intra- and intermolecular Se...X(X= Se, O) interactions in selenium-containing heterocycles: 3-benzoylimino-5-(morpholin-4-yl)-1,2,4-diselenazole

Linden, Anthony ; Zhou, Yuehui ; Heimgartner, Heinz

Abstract: In the selenium-containing heterocyclic title compound {systematic name: N-[5-(morpholin-4-yl)-3H-1,2,4-diselenazol-3-ylidene]benzamide, C13H13N3O2Se2, the five-membered 1,2,4-diselenazole ring and the amide group form a planar unit, but the phenyl ring plane is twisted by 22.12 (19)° relative to this plane. The five consecutive N-C bond lengths are all of similar lengths [1.316 (6)-1.358 (6) Å], indicating substantial delocalization along these bonds. The Se...O distance of 2.302 (3) Å, combined with a longer than usual amide C=O bond of 2.252 (5) Å, suggest a significant interaction between the amide O atom and its adjacent Se atom. An analysis of related structures containing an Se-Se...X unit (X = Se, S, O) shows a strong correlation between the Se-Se bond length and the strength of the Se...X interaction. When X = O, the strength of the Se...O interaction also correlates with the carbonyl C=O bond length. Weak intermolecular Se...Se, Se...O, C-H...O, C-H...[pi] and [pi]-[pi] interactions each serve to link the molecules into ribbons or chains, with the C-H...O motif being a double helix, while the combination of all interactions generates the overall three-dimensional supramolecular framework.

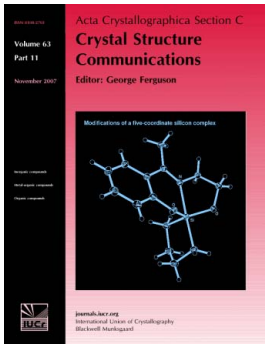
DOI: https://doi.org/10.1107/S2053229614008237

Acta Crystallographica Section C
Structural Chemistry
ISSN 2053-2296

Intra- and intermolecular Se···*X* (*X* = Se, O) interactions in selenium-containing heterocycles: 3-benzoylimino-5-(morpholin-4-yl)-1,2,4-diselenazole

Anthony Linden, Yuehui Zhou and Heinz Heimgartner

Acta Cryst. (2014). C**70**, 482–487



Acta Crystallographica Section C: Structural Chemistry specializes in the rapid dissemination of high-quality detailed studies of novel and challenging crystal and molecular structures of interest in the fields of chemistry, biochemistry, mineralogy, pharmacology, physics and materials science. The unique checking, editing and publishing facilities of the journal ensure the highest standards of structural reliability and presentation, while providing for reports on studies involving special techniques or difficult crystalline materials. Papers go beyond reporting the principal numerical and geometrical data, and may include the discussion of multiple related structures, a detailed description of non-routine structure determinations, placing the structure in an interesting scientific, physical or chemical context, or the discussion of interesting physical properties or modes of association. Reports of difficult or challenging structures, such as cases of twinning, severe disorder, or diffuse solvent regions are welcomed, provided the presented structures are correct and the difficulties and strategies used to treat them are scientifically discussed and properly documented. *Section C* readers have access to an extensive back archive of high-quality structural data.

Acta Crystallographica Section C
Structural Chemistry
ISSN 2053-2296

Intra- and intermolecular Se···*X* (*X* = Se, O) interactions in selenium-containing heterocycles: 3-benzoylimino-5-(morpholin-4-yl)-1,2,4-diselenazole

Anthony Linden,[a]* Yuehui Zhou[b] and Heinz Heimgartner[a]

[a]Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland, and [b]Jingsu Pioneer Biotechnology Research Centre, 403 Chenghuang Road, Huangqiao, Taixing, People's Republic of China
Correspondence e-mail: anthony.linden@chem.uzh.ch

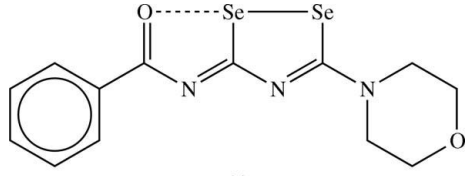
Received 1 April 2014
Accepted 11 April 2014

In the selenium-containing heterocyclic title compound {systematic name: *N*-[5-(morpholin-4-yl)-3*H*-1,2,4-diselenazol-3-ylidene]benzamide}, $C_{13}H_{13}N_3O_2Se_2$, the five-membered 1,2,4-diselenazole ring and the amide group form a planar unit, but the phenyl ring plane is twisted by 22.12 (19)° relative to this plane. The five consecutive N—C bond lengths are all of similar lengths [1.316 (6)–1.358 (6) Å], indicating substantial delocalization along these bonds. The Se···O distance of 2.302 (3) Å, combined with a longer than usual amide C=O bond of 2.252 (5) Å, suggest a significant interaction between the amide O atom and its adjacent Se atom. An analysis of related structures containing an Se—Se···*X* unit (*X* = Se, S, O) shows a strong correlation between the Se—Se bond length and the strength of the Se···*X* interaction. When *X* = O, the strength of the Se···O interaction also correlates with the carbonyl C=O bond length. Weak intermolecular Se···Se, Se···O, C—H···O, C—H···π and π–π interactions each serve to link the molecules into ribbons or chains, with the C—H···O motif being a double helix, while the combination of all interactions generates the overall three-dimensional supramolecular framework.

Keywords: crystal structure; selenium-containing heterocycles; 1,2,4-diselenazoles; double helix; supramolecular framework; intermolecular interactions; hydrogen bonding; Se···O interactions.

1. Introduction

Isoselenocyanates are very useful synthons for the preparation of selenium-containing heterocycles (Garud *et al.*, 2007; Heimgartner *et al.*, 2008; Ninomiya *et al.*, 2010). Whereas aryl and benzimidoyl isoselenocyanates have been isolated and characterized spectroscopically or by X-ray crystallography (*e.g.* Barton *et al.*, 1994; Koketsu *et al.*, 2007; Zakrzewski & Krawczyk, 2009; Atanassov *et al.*, 2002), benzoyl isoselenocyanates are unstable and have been characterized *via* their reaction with primary and secondary amines, leading to *N*-benzoylselenoureas (*e.g.* Douglass, 1937; Köhler *et al.*, 1990; Zhou & Heimgartner, 2000). Aroyl isoselenocyanates generated *in situ* have also been trapped with diphenyldiazomethane (L'abbé *et al.*, 1980) and ethyl diazoacetate (Zhou & Heimgartner, 2000). Benzoyl isoselenocyanates are generated by the reaction of benzoyl chlorides with potassium selenocyanate. In the presence of diethylamine, 3-benzoyl-1,1-diethylselenourea (21%) and 2-benzoylamino-5-diethylamino-1,6,6aλ^4-triselena-3,4-diazapentalene (4.8%) were obtained (Köhler *et al.*, 1990). The structure of the latter, containing fused 1,2,4-diselenazole rings with a tetravalent Se atom, was established by X-ray crystallography (Richter *et al.*, 1991). In contrast with the corresponding sulfur analogues, 1,2,4-diselenazole derivatives have rarely been described (Burger & Ottlinger, 1978; Liebscher *et al.*, 1979; Shibuya, 1986, 1987; Rosenbaum *et al.*, 1992). In the case of 3-dimethylamino-5-phenyl-1,2,4-diselenazolium tetrachloronickelate, a crystal structure is available (Rosenbaum *et al.*, 1992). The title compound, (I), was obtained unexpectedly as an uncharacterized side-product. The one-pot reaction of benzoyl chloride, potassium selenocyanate and ethyl diazoacetate (Zhou & Heimgartner, 2000), after treatment with morpholine, gave *N*-[(morpholin-4-yl)selenocarbonyl]benzamide and 3-benzoylimino-5-(morpholin-4-yl)-1,2,4-diselenazole, (I). The latter can be prepared in up to 20% yield by treatment of the reaction mixture of benzoyl chloride and potassium selenocyanate with morpholine. The crystal structure of (I) was initially determined in order to characterize this unexpected product, and the structure shows interesting intra- and intermolecular Se···O and Se···Se interactions.



(I)

2. Experimental

2.1. Synthesis and crystallization

The title compound was prepared by analogy with an earlier described procedure (Zhou & Heimgartner, 2000), by treatment of the noncharacterized oligomeric material obtained from the three-component reaction of benzoyl chloride, potassium selenocyanate and ethyl diazoacetate in acetone, and suspended in dichloromethane, with excess morpholine at room temperature. The yellow–green crystals of the major product, *N*-[(morpholin-4-yl)selenocarbonyl]benzamide, and the orange–yellow crystals of 3-benzoylimino-5-(morpholin-4-yl)-1,2,4-diselenazole, (I) (yield 5–10%), were separated by hand and the latter were recrystallized from ethanol at room temperature.

  doi:10.1107/S2053229614008237

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{13}H_{13}N_3O_2Se_2$
M_r	401.18
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	160
a, b, c (Å)	13.923 (5), 6.807 (4), 15.166 (5)
β (°)	95.76 (3)
V (Å^3)	1430.0 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.18
Crystal size (mm)	0.50 × 0.42 × 0.17
Data collection	
Diffractometer	Rigaku AFC-5R diffractometer
Absorption correction	ψ scan (North *et al.*, 1968)
T_{min}, T_{max}	0.183, 0.415
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3406, 3275, 2135
R_{int}	0.023
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.092, 1.02
No. of reflections	3275
No. of parameters	181
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.60, −0.47

Computer programs: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991), *TEXSAN* (Molecular Structure Corporation, 1999), *SHELXS97* (Sheldrick, 2008), *ORTEPII* (Johnson, 1976), *Mercury* (Macrae *et al.*, 2008), *SHELXL2013* (Sheldrick, 2013), *publCIF* (Westrip, 2010) and *PLATON* (Spek, 2009).

Alternatively, a mixture of benzoyl chloride (*ca* 0.02 mmol) and potassium selenocyanate (1.1 mole equivalents) in acetone (30–40 ml) was stirred for 1 h. Then, morpholine (5 mole equivalents) was added and the mixture stirred for another 1 h. The orange–yellow crystals which formed were separated manually and recrystallized from ethanol at room temperature to give 3-benzoylimino-5-(morpholin-4-yl)-1,2,4-diselenazole, (I) (yield 10–20%).

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.95 (aromatic) or 0.99 Å (methylene) and U_{iso}(H) = 1.2U_{eq}(C).

3. Results and discussion

The 1,2,4-diselenazole ring in the crystal structure of (I) is planar, with an r.m.s. deviation for the ring atoms of 0.036 Å and a maximum deviation from the mean plane of 0.035 (5) Å for atom C3 (Fig. 1). The adjacent morpholine ring atoms N3, C4 and C7, as well as the atoms of the amide group (N1, C1, O1 and C8), deviate only slightly from this plane, with the maximum deviation being 0.120 (5) Å for atom C4. The mean plane through these 12 atoms has an r.m.s. deviation of 0.052 Å and a maximum deviation from the mean plane of 0.076 (3) Å for atom O1. In contrast, the plane of the phenyl ring is twisted somewhat relative to the plane of the 1,2,4-diselenazole ring, with a dihedral angle between the two ring planes of 22.12 (19)°. The morpholine ring exists in a chair conformation. The similarity of the five consecutive C—N bond lengths from C1 through to N3, which are in the range 1.316 (6)–1.358 (6) Å, indicates a delocalized π-system (Table 2). The longest C—N bond is that of the amide group, while all others fall within a range of 0.02 Å.

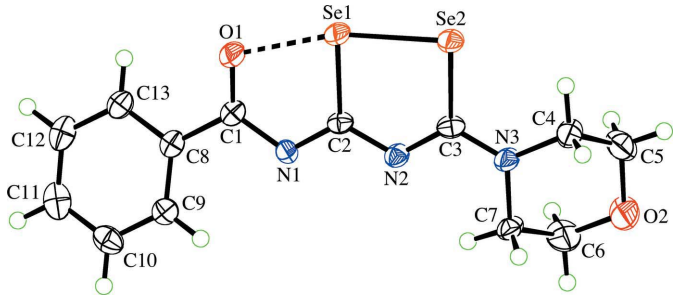


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates the Se···O interaction.

The bond lengths within the 1,2,4-diselenazole ring (Table 2) are comparable with those in 3-dimethylamino-5-phenyl-1,2,4-diselenazolium tetrachloroniccolate (Rosenbaum *et al.*, 1992), although the Se—Se bond in (I) is about 0.09 Å longer than that in the earlier report [2.293 (1) Å]. There are no other structures containing an unfused 1,2,4-diselenazole ring recorded in the Cambridge Structural Database (CSD, Version 5.35 of 2013 plus two updates; Allen, 2002), although a structure incorporating a 1,2,4-diselenazolidine ring (all bonds in the ring are saturated; Takikawa *et al.*, 1995, 2006) has an Se—Se distance of 2.331 (2) Å, while the Se—C and C—N bonds are about 0.15 and 0.07 Å longer, respectively, than those in the 1,2,4-diselenazoles.

The CSD lists 50 entries involving the 1,2-diselenole ring for which atomic coordinates are available. This ring is analogous to the 1,2,4-diselenazole ring, with the N atom replaced by a C atom. In these structures, the Se—Se distances fall in the range 2.30–2.53 Å, with a mean of 2.347 (4) Å, and only five of these have distances greater than 2.37 Å, which occurs when the ring is fused with both rings of a naphthyl unit. Perhaps the closest analogue amongst these to the 1,2,4-diselenazole structures is *N*-[(3*Z*)-5-phenyl-3*H*-1,2-diselenol-3-ylidene]aniline, in which the Se—Se distance is 2.3325 (8) Å (Shimada *et al.*, 2007) and the Se—C distances are very similar to those in the structures with 1,2,4-diselenazole rings.

Table 2
Selected geometric parameters (Å, °).

Se1—Se2	2.3818 (11)	N1—C1	1.358 (6)
Se1—C2	1.926 (4)	N1—C2	1.320 (5)
Se1—O1	2.302 (3)	N2—C2	1.337 (5)
Se2—C3	1.897 (4)	N2—C3	1.316 (6)
O1—C1	1.252 (5)	N3—C3	1.331 (6)
Se2—Se1—O1	164.75 (8)	Se1—Se2—C3	88.90 (15)
Se2—Se1—C2	88.74 (14)	C1—O1—Se1	104.8 (3)
O1—Se1—C2	76.05 (16)		

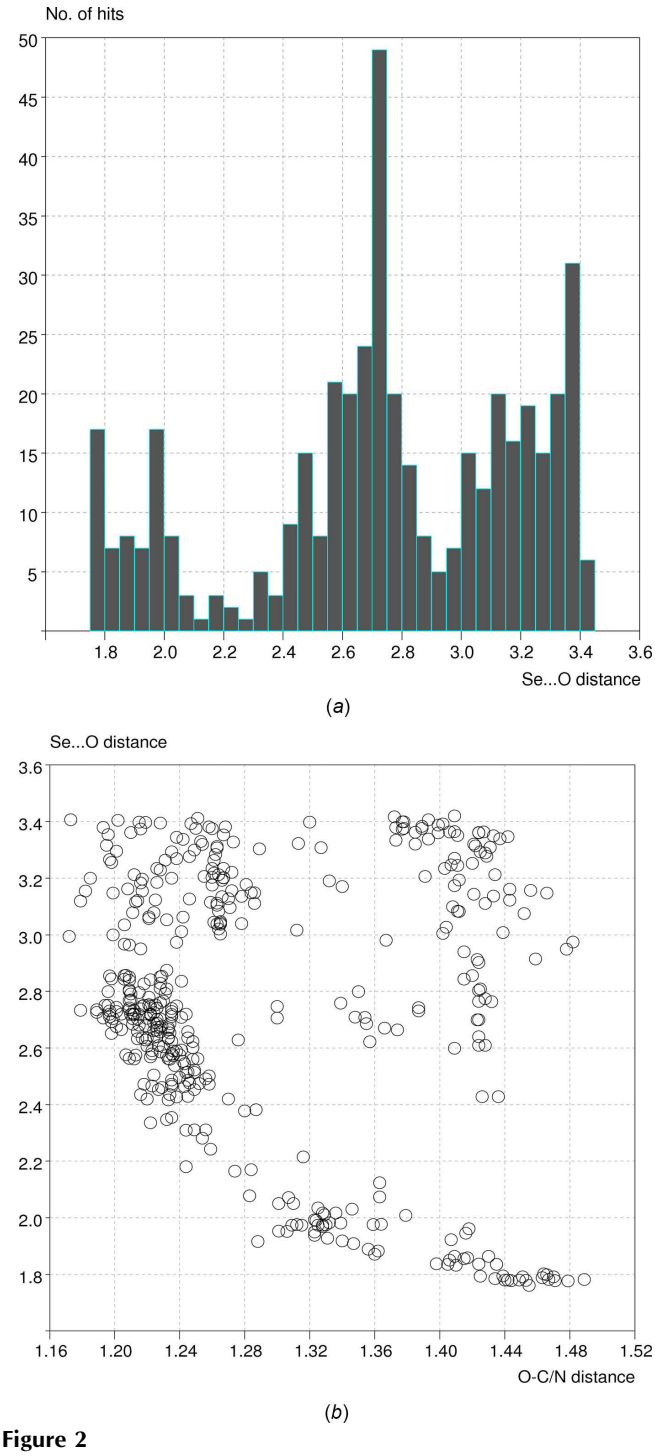


Figure 2
An analysis of intramolecular Se···O interactions in structures contained in the CSD. (*a*) A histogram of Se···O distances shorter than the sum of the Se and O van der Waals radii. (*b*) A scatter plot showing the correlation between the Se···O distance and the length of a neighbouring C═O or O—N bond.

The distance between amide atom O1 of (I) and the adjacent Se1 atom is 2.302 (3) Å, which is substantially shorter than the sum of the van der Waals radii of these atoms (3.42 Å; Bondi, 1964) but, as noted by Busetti *et al.* (1978), longer than the sum of the covalent radii of these atoms (1.91 Å; Pauling, 1960). The C1—O1 distance of 1.252 (5) Å is also longer than that of a normal carbonyl bond. It may thus be concluded that there is a significant interaction between atoms Se1 and O1. A closely related structure with the same Se—Se···O arrangement as part of two fused five-membered rings is that of 2,5-dimethyl-1,2-diselenolo[1,5-*b*][1,2]oxaselenole (Busetti *et al.*, 1978), in which the O—Se and Se—Se distances are 2.336 (15) and 2.384 (3) Å, respectively. Similar Se···O distances have been observed in *o*-formylphenylselenenyl bromide [2.305 (19) Å; Baiwir *et al.*, 1975], in *o*-carboxyphenylmethylselenium oxide [2.378 (3) Å; Dahlén, 1973] and in ethyl 2-(4-methylbenzoyl)-5-[(4-methylbenzoyl)imino]-2,5-dihydro-1,2,3-selenadiazole-4-carboxylate [2.242 (2) Å; Zhou & Heimgartner, 2000], although these compounds do not possess a diselenium unit. This last compound also has a long carbonyl bond of 1.259 (4) Å, similar to that in (I). Another closely related structure with the same Se—Se···O arrangement is 3,4-dimethyl-1-oxa-6,6aλ^4-diselena-2-azapentalene (Allen *et al.*, 1987). However, in this case the O atom is not part of a carbonyl group but is bonded to an N atom. The O···Se and Se···Se distances, averaged over two independent molecules, are 2.043 (8) and 2.444 (2) Å, respectively, which suggests a stronger Se···O bonding interaction than in the other compounds described above.

The CSD produces 436 hits (274 structures) for molecules containing an intramolecular Se···O distance less than the van der Waals radii sum, with the Se and O atoms being otherwise bonded *via* three intervening C and/or N atoms. Fig. 2(*a*) shows that the distances are clustered into three regions. The region below about 2.05 Å can be considered to represent normal Se—O covalent bonds. The middle region centred around 2.6–2.8 Å seems to result from arrangements where geometric constraints, such as intervening aromatic systems or fused rings, force the Se and O atoms to lie this far apart. The region beyond 3.0 Å likely represents unimportant intramolecular contacts. A scatterplot of the Se···O distance *versus* the length of the C—O or N—O bond to the O atom shows a strong correlation between the Se···O and O—C/N distances when the Se···O distance is shorter than about 2.9 Å. Short Se···O and long O—C/N distances (lower right of Fig. 2*b*) represent normal covalent Se—O—C/N single bonds. Se···O distances near 2.8 Å correspond to normal carbonyl C═O double bonds (middle left of Fig. 2*b*), thereby suggesting there is no significant bonding interaction between the Se and O atoms in such cases. In between, decreasing Se···O distances correlate with increasing O—C/N distances, which suggests an increasing degree of Se···O bonding interaction. While examples with Se···O distances of 2.1–2.4 Å are not very common, the Se1···O1 distance of 2.302 (3) Å in (I) and similar values in the other examples mentioned above are completely consistent with the trend shown in Fig. 2(*b*).

It is instructive to examine other structures with two fused five-membered rings sharing a common Se atom and the same Se—Se···*X* (*X* = O, S, Se) arrangement present in (I), and to compare the Se—Se and Se···*X* distances. There is a trend that the Se—Se bond is longer if one of the Se atoms is bonded to or interacting with *X*. In 6a-selenaselenophthene (Hordvik & Julshamn, 1971), which has an Se—Se—Se unit, the two

Se—Se bonds are 2.579 (3) and 2.586 (3) Å. Four other related triselena compounds are listed in the CSD and have Se—Se bond lengths in the range 2.56–2.64 Å. Two compounds are listed in the CSD in which X = S: 3,5-diphenyl-2-(2-pyridylamino)-1-thia-6,6aλ^4-diselenapentalene (Billing *et al.*, 1995) and 2,4-dimethyl-1-thia-6,6aλ^4-diselena-3-azapentalene (Allen *et al.*, 1987) have Se—Se distances in the range 2.47–2.49 Å, clearly shorter than in the triselena compounds. Interestingly, the Se—S distances in these compounds are almost the same as the Se—Se distances (2.49–2.50 Å). The three known cases with X = O have already been mentioned above and here the Se—Se distances are shorter again [2.3818 (11) Å for (I), 2.384 (3) Å in Busetti *et al.* (1978) and 2.444 (2) Å in Allen *et al.* (1987)] than in the cases with X = Se or S. Given that Se—Se bonds in pure 1,2,4-diselenazole rings, where there is no adjacent X atom and no fusing with naphthyl rings, are in the range 2.29–2.37 Å, the trend in Se—Se distances for different X follows the sequence Se > S > O $\simeq$ none, which appears to correlate well with the strength of the adjacent Se$\cdots X$ interaction.

There is a broad palette of weak intermolecular contacts comprising the supramolecular structure of (I). The motif generated by each type of interaction will be described separately, and then how these combine to give the overall supramolecular network will be assessed. A C—H$\cdots$O interaction links the *meta*-C—H group of the phenyl ring to the morpholine O atom of a neighbouring molecule, which is related to the reference molecule by the 2_1 screw axis at $x = 0$, $z = \frac{1}{4}$ [H10$\cdots$O2^{i} = 2.47 Å, C10$\cdots$O2^{i} = 3.375 (7) Å and C10—H10$\cdots$O2^{i} = 160°; symmetry code: (i) $-x$, $y - \frac{3}{2}$, $-z + \frac{1}{2}$]. Propagation of this end-to-end interaction leads to zigzag chains of molecules which lie parallel to the [010] direction (Fig. 3). The graph-set descriptor (Bernstein *et al.*, 1995) for this interaction is $C(13)$. Two such chains intertwine along the same 2_1 screw axis to give a double helix with a pitch of $2b$ [13.614 (8) Å] (Fig. 4). The individual strands within the double helix appear to be linked to one another *via* further weak interactions, as will be detailed below.

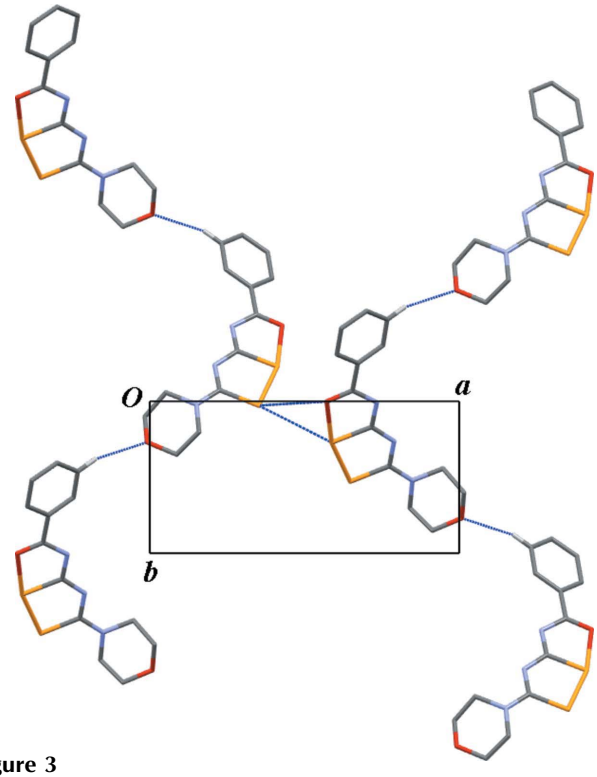


Figure 3
A view of (I) along [001], showing two individual C—H$\cdots$O hydrogen-bonded strands from two adjacent double helices and the connection between them *via* Se$\cdots$Se and Se$\cdots$O interactions. The intermolecular interactions are shown as blue dotted lines. H atoms not involved in the displayed interactions have been omitted.

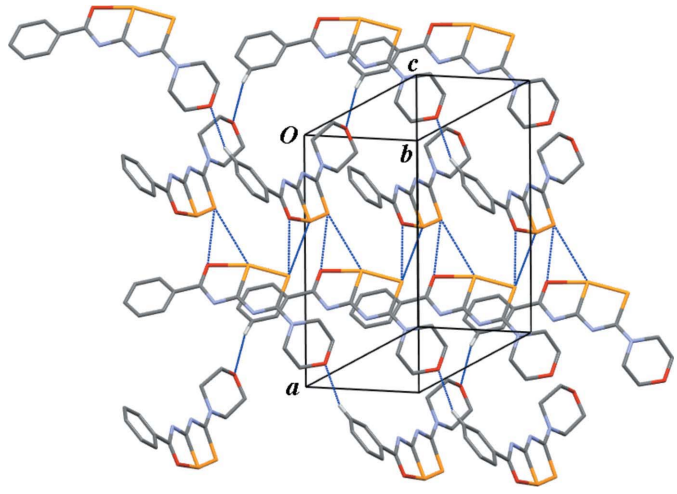


Figure 4
A view of the crystal packing in (I), showing two C—H$\cdots$O hydrogen-bonded double helices (upper and lower halves of the image) connected by Se$\cdots$Se and Se$\cdots$O interactions to give layers parallel to (001). The intermolecular interactions are shown as blue dotted lines. H atoms not involved in the displayed interactions have been omitted.

Atom Se2 has a short contact with atoms Se1 and O2 of a neighbouring molecule, with Se2$\cdots$Se1^{ii} and Se2$\cdots$O1^{ii} distances of 3.697 (2) and 3.177 (3) Å, respectively [symmetry code: (ii) $-x + 1$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$]. These interactions are 0.10 and 0.24 Å, respectively, shorter than the sums of the van der Waals radii of the involved atoms (Bondi, 1964). In this way, the corner Se2 atom of the Se—Se$\cdots$O group appears to be pointing towards the Se1$\cdots$O1 'bond' of a neighbouring molecule, which is related to the reference molecule by the 2_1 screw axis at $x = \frac{1}{2}$, $z = \frac{1}{4}$ (Fig. 3). Propagation of these weak interactions leads to zigzag ribbons of molecules, which also lie parallel to the [010] direction and have the Se-rich components of the molecules aligned along the centre line of the ribbon (Fig. 4). These interactions play a further dual role, firstly as crosslinks between adjacent C—H$\cdots$O hydrogen-bonded double helices, thereby generating puckered or herringbone-patterned layers which lie parallel to the (001) plane (Fig. 5), and secondly as an external link between the individual strands within the double helix. This external link arises because the outer Se atom of the Se—Se$\cdots$O unit interacts with the middle Se and outer O atoms from one of the helical strands in an adjacent double helix, and the Se$\cdots$O unit interacts with the outer Se atom of the other helical strand in the same adjacent double helix.

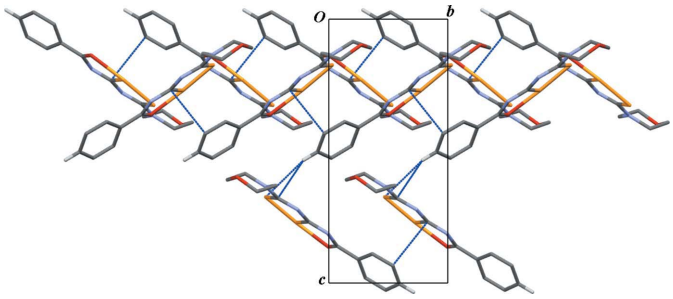


Figure 5
A view of (I) along [100], showing a side-on view of one layer built from the C—H···O hydrogen-bonded and Se···Se/Se···O crosslinked double helices. The C—H···π interactions between this layer and just two molecules in the next layer are shown, as are the π–π interactions between the phenyl rings and the five-membered ring containing atom Se2. In each case, the blue dotted lines represent the shortest contacts within these two types of interaction. H atoms not involved in the displayed interactions have been omitted.

Weak intermolecular Se···Se interactions in organic molecules have been discussed by Lari *et al.* (2009). The CSD currently lists 973 hits (530 structures) for intermolecular Se···Se contacts of less than 3.80 Å involving non-ionic compounds not containing Se^+ or other metals and for which coordinates are available. The vast majority (87%) of these have Se···Se distances greater than 3.4 Å and the distance observed for (I) is longer than 64% of the hits, so is not unusual. The shortest Se···Se contact of 2.93 Å can be found in the structure of 1,3-selenazolidine-2,4-dione (Levshin *et al.*, 1982).

A potential weak C—H···π interaction can be discerned in (I) between C11—H11 of the phenyl ring and the five-membered ring containing both Se atoms of a neighbouring molecule, although the C—H vector appears to point more directly at the Se2—C3 bond (Fig. 5). The H11···Se2^{iii} and H11···C3^{iii} distances are 3.09 and 2.86 Å, respectively (just at the van der Waals limit), while the C11—H11···Se2^{iii} and C11—H11···C3^{iii} angles are both 153° [symmetry code: (iii) x, $-y+\frac{1}{2}$, $z+\frac{1}{2}$]. The H11···*Cg*1^{iii} distance is 2.97 Å and the C11—H11···*Cg*1^{iii} angle is 137°, where *Cg*1 is the centre of gravity of the ring containing atoms Se1/Se2/C3/N2/C2. This interaction serves to link the molecules into herringbone-shaped zigzag chains which run parallel to the [001] direction. Overall, the combination of this and the C—H···O and Se···O/Se···Se interactions yields a three-dimensional supramolecular framework.

Finally, a very weak π–π interaction might exist between the five-membered ring defining *Cg*1 and the phenyl ring of an adjacent molecule (centre of gravity = *Cg*2), although the inclination of the two rings is quite severe. The *Cg*1···*Cg*2^{iv} distance is 3.915 (3) Å and the dihedral angle between the ring planes is 22.12 (19)° [symmetry code: (iv) x, $y+1$, z]. This interaction provides a further connection between the individual strands within the hydrogen-bonded double helix described above (Fig. 5).

Although compound (I) was obtained serendipitously, its crystal structure has permitted a consistent analysis of information concerning intra- and intermolecular Se···*X* interactions involving the Se—Se···*X* unit (*X* = Se, S, O) for a sparsely populated class of selenium-containing heterocyclic compounds.

Supporting information for this paper is available from the IUCr electronic archives (Reference: KY3053).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Allen, C., Boeyens, J. C. A., Briggs, A. G., Denner, L., Markwell, A. J., Reid, D. H. & Rose, B. G. (1987). *J. Chem. Soc. Chem. Commun.* pp. 967–968.
Atanassov, P. K., Zhou, Y., Linden, A. & Heimgartner, H. (2002). *Helv. Chim. Acta*, **85**, 1102–1117.
Baiwir, M., Llabres, G., Dideberg, O., Dupont, L. & Piette, J. L. (1975). *Acta Cryst.* B**31**, 2188–2191.
Barton, D. H. R., Parekh, S. I., Tajbakhsh, M., Theodorakis, E. A. & Tse, C. L. (1994). *Tetrahedron*, **50**, 639–654.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Billing, D. G., Levendis, D. C., Reid, D. H. & Rose, B. G. (1995). *Acta Cryst.* C**51**, 2057–2059.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Burger, K. & Ottlinger, R. (1978). *Tetrahedron Lett.* pp. 973–976.
Busetti, V., Valle, G. & Bardi, R. (1978). *Acta Cryst.* B**34**, 691–693.
Dahlén, B. (1973). *Acta Cryst.* B**29**, 595–602.
Douglass, I. B. (1937). *J. Am. Chem. Soc.* **59**, 740–742.
Garud, D. R., Koketsu, M. & Ishihara, H. (2007). *Molecules*, **12**, 504–535.
Heimgartner, H., Zhou, Y., Atanassov, P. K. & Sommen, G. L. (2008). *Phosphorus Sulfur Silicon Relat. Elem.* **183**, 840–855.
Hordvik, A. & Julshamn, K. (1971). *Acta Chem. Scand.* **25**, 2507–2515.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Köhler, R., Beyer, L., Moll, M., Hantschmann, A., Richter, R., Sieler, J., Szargan, R., Weber, L. & Hoyer, E. (1990). *Tetrahedron*, **46**, 7735–7738.
Koketsu, M., Takahashi, A. & Ishihara, H. (2007). *J. Heterocycl. Chem.* **44**, 79–81.
L'abbé, G., Dekerk, J.-P., Martens, C. & Toppet, S. (1980). *J. Org. Chem.* **45**, 4366–4371.
Lari, A., Bleiholder, C., Rominger, F. & Gleiter, R. (2009). *Eur. J. Org. Chem.* pp. 2765–2774.
Levshin, I. B., Kaganskii, M. M., V'yunov, K. A., Tsurkan, A. A., Ginak, A. I., Espenbetov, A. A., Yanovsky, A. I. & Struchkov, Yu. T. (1982). *J. Appl. Spectrosc.* **37**, 813–816.
Liebscher, J., Hantschmann, A. & Hartmann, H. (1979). German Democratic Republic Patent DD 134093 A1 19790207.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software*. MSC, The Woodlands, Texas, USA.
Molecular Structure Corporation (1999). *TEXSAN*. MSC, The Woodlands, Texas, USA.
Ninomiya, M., Garud, D. R. & Koketsu, M. (2010). *Heterocycles*, **81**, 2027–2055.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Pauling, L. (1960). In *The Nature of the Chemical Bond*. Ithaca: Cornell University Press.
Richter, R., Sieler, J., Hansen, L. K., Köhler, R., Beyer, L. & Hoyer, E. (1991). *Acta Chem. Scand.* **45**, 1–5.
Rosenbaum, K., Beyer, L., Richter, R. & Hoyer, E. (1992). *Z. Anorg. Allg. Chem.* **617**, 89–92.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2013). *SHELXL2013*. University of Göttingen, Germany.
Shibuya, I. (1986). Jpn Patent JP 61205269 A 19860911.
Shibuya, I. (1987). *Nippon Kagaku Kaishi*, pp. 1691–1694.
Shimada, K., Moro-oka, A., Maruyama, A., Fujisawa, H., Saito, T., Kawamura, R., Kogawa, H., Sakuraba, M., Aoyagi, S., Takikawa, Y. & Kabuto, C. (2007). *Bull. Chem. Soc. Jpn*, **80**, 567–577.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Takikawa, Y., Koyama, Y., Yoshida, T., Makino, K., Shibuya, H., Sato, K., Otsuka, T., Shibata, Y., Onuma, Y., Aoyagi, S., Shimada, K. & Kabuto, C. (2006). *Bull. Chem. Soc. Jpn*, **79**, 1913–1925.

Takikawa, Y., Yoshida, T., Koyama, Y. & Shimada, K. (1995). *Chem. Lett.* pp. 277–278.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Zakrzewski, J. & Krawczyk, M. (2009). *Phosphorus Sulfur Silicon Relat. Elem.* **183**, 1880–1903.
Zhou, Y. & Heimgartner, H. (2000). *Helv. Chim. Acta*, **83**, 539–553.

supplementary materials

Acta Cryst. (2014). C**70**, 482-487 [doi:10.1107/S2053229614008237]

Intra- and intermolecular Se···*X* (*X* = Se, O) interactions in selenium-containing heterocycles: 3-benzoylimino-5-(morpholin-4-yl)-1,2,4-diselenazole

Anthony Linden, Yuehui Zhou and Heinz Heimgartner

Computing details

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2013); molecular graphics: *ORTEPII* (Johnson, 1976) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2013* (Sheldrick, 2013), *publCIF* (Westrip, 2010) and *PLATON* (Spek, 2009)′.

N-[5-(morpholin-4-yl)-3*H*-1,2,4-diselenazol-3-ylidene]benzamide

Crystal data

$C_{13}H_{13}N_3O_2Se_2$
M_r = 401.18
Monoclinic, $P2_1/c$
a = 13.923 (5) Å
b = 6.807 (4) Å
c = 15.166 (5) Å
β = 95.76 (3)°
V = 1430.0 (10) Å^3
Z = 4
$F(000)$ = 784
D_x = 1.863 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 39.4–39.9°
μ = 5.18 mm^{-1}
T = 160 K
Prism, orange-yellow
0.50 × 0.42 × 0.17 mm

Data collection

Rigaku AFC-5R diffractometer
Radiation source: Rigaku rotating anode generator
Graphite monochromator
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.183, T_{max} = 0.415
3406 measured reflections
3275 independent reflections
2135 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 27.5°, θ_{min} = 2.7°
h = 0→18
k = 0→8
l = −19→19
3 standard reflections every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.092
S = 1.02
3275 reflections
181 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 0.7378P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}

Special details

Experimental. Solvent used: EtOH

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Se1	0.41226 (3)	0.77208 (7)	0.27089 (3)	0.03025 (14)
Se2	0.35195 (3)	1.02891 (7)	0.17399 (3)	0.03072 (14)
O1	0.4278 (2)	0.5025 (5)	0.3629 (2)	0.0355 (8)
O2	−0.0084 (3)	1.2703 (6)	0.0983 (3)	0.0597 (12)
N1	0.2661 (3)	0.5080 (5)	0.3114 (2)	0.0260 (8)
N2	0.2102 (3)	0.7635 (6)	0.2209 (2)	0.0255 (8)
N3	0.1511 (3)	1.0215 (6)	0.1360 (3)	0.0318 (9)
C1	0.3447 (3)	0.4306 (7)	0.3593 (3)	0.0256 (10)
C2	0.2829 (3)	0.6698 (6)	0.2675 (3)	0.0235 (10)
C3	0.2257 (3)	0.9274 (7)	0.1786 (3)	0.0265 (10)
C4	0.1594 (3)	1.2028 (8)	0.0852 (3)	0.0383 (13)
H41	0.1490	1.1733	0.0210	0.046*
H42	0.2252	1.2575	0.0980	0.046*
C5	0.0866 (4)	1.3510 (8)	0.1088 (4)	0.0486 (15)
H51	0.1024	1.3934	0.1710	0.058*
H52	0.0893	1.4679	0.0703	0.058*
C6	−0.0154 (4)	1.1014 (8)	0.1531 (4)	0.0474 (15)
H61	−0.0824	1.0508	0.1456	0.057*
H62	−0.0003	1.1392	0.2160	0.057*
C7	0.0522 (3)	0.9433 (7)	0.1304 (3)	0.0307 (11)
H71	0.0494	0.8320	0.1721	0.037*
H72	0.0330	0.8946	0.0697	0.037*
C8	0.3276 (3)	0.2498 (6)	0.4102 (3)	0.0250 (10)
C9	0.2463 (3)	0.1331 (7)	0.3891 (3)	0.0284 (10)
H9	0.1993	0.1728	0.3428	0.034*
C10	0.2326 (4)	−0.0374 (7)	0.4338 (3)	0.0356 (12)
H10	0.1776	−0.1168	0.4176	0.043*
C11	0.2993 (4)	−0.0935 (8)	0.5025 (3)	0.0400 (13)
H11	0.2896	−0.2112	0.5340	0.048*
C12	0.3807 (4)	0.0205 (8)	0.5261 (3)	0.0377 (12)
H12	0.4262	−0.0190	0.5736	0.045*
C13	0.3952 (3)	0.1921 (7)	0.4799 (3)	0.0305 (11)
H13	0.4508	0.2702	0.4956	0.037*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Se1	0.0177 (2)	0.0341 (3)	0.0387 (3)	−0.0006 (2)	0.00180 (19)	0.0044 (2)
Se2	0.0211 (2)	0.0347 (3)	0.0366 (3)	−0.0040 (2)	0.0040 (2)	0.0071 (2)
O1	0.0230 (17)	0.037 (2)	0.045 (2)	0.0007 (15)	0.0002 (15)	0.0096 (16)
O2	0.026 (2)	0.045 (2)	0.110 (4)	0.0092 (18)	0.015 (2)	0.017 (2)
N1	0.024 (2)	0.021 (2)	0.033 (2)	−0.0003 (16)	0.0030 (17)	0.0031 (17)
N2	0.0198 (18)	0.030 (2)	0.027 (2)	0.0012 (17)	0.0042 (16)	0.0014 (17)
N3	0.0200 (19)	0.038 (2)	0.037 (2)	−0.0039 (18)	0.0002 (17)	0.0134 (19)
C1	0.024 (2)	0.030 (3)	0.023 (2)	0.004 (2)	0.0034 (19)	−0.002 (2)
C2	0.019 (2)	0.027 (2)	0.025 (2)	−0.0002 (18)	0.0050 (18)	−0.0047 (19)
C3	0.021 (2)	0.034 (3)	0.025 (2)	−0.003 (2)	0.0065 (19)	−0.002 (2)
C4	0.025 (3)	0.044 (3)	0.047 (3)	0.000 (2)	0.007 (2)	0.020 (3)
C5	0.039 (3)	0.031 (3)	0.078 (4)	−0.003 (2)	0.015 (3)	0.003 (3)
C6	0.034 (3)	0.050 (3)	0.062 (4)	−0.003 (3)	0.020 (3)	0.005 (3)
C7	0.019 (2)	0.040 (3)	0.033 (3)	−0.001 (2)	0.001 (2)	0.008 (2)
C8	0.025 (2)	0.029 (3)	0.021 (2)	0.006 (2)	0.0061 (18)	−0.004 (2)
C9	0.030 (3)	0.029 (2)	0.026 (2)	0.003 (2)	0.004 (2)	−0.006 (2)
C10	0.039 (3)	0.029 (3)	0.040 (3)	−0.002 (2)	0.012 (2)	−0.008 (2)
C11	0.048 (3)	0.039 (3)	0.037 (3)	0.012 (3)	0.022 (3)	0.006 (2)
C12	0.037 (3)	0.047 (3)	0.030 (3)	0.014 (3)	0.008 (2)	0.006 (2)
C13	0.026 (2)	0.035 (3)	0.032 (3)	0.007 (2)	0.006 (2)	−0.002 (2)

Geometric parameters (Å, º)

Se1—Se2	2.3818 (11)	C5—H51	0.9900
Se1—C2	1.926 (4)	C5—H52	0.9900
Se1—O1	2.302 (3)	C6—C7	1.492 (7)
Se2—C3	1.897 (4)	C6—H61	0.9900
O1—C1	1.252 (5)	C6—H62	0.9900
O2—C5	1.427 (6)	C7—H71	0.9900
O2—C6	1.428 (6)	C7—H72	0.9900
N1—C1	1.358 (6)	C8—C9	1.393 (6)
N1—C2	1.320 (5)	C8—C13	1.400 (6)
N2—C2	1.337 (5)	C9—C10	1.366 (6)
N2—C3	1.316 (6)	C9—H9	0.9500
N3—C3	1.331 (6)	C10—C11	1.378 (7)
N3—C4	1.465 (6)	C10—H10	0.9500
N3—C7	1.470 (6)	C11—C12	1.390 (8)
C1—C8	1.485 (6)	C11—H11	0.9500
C4—C5	1.499 (7)	C12—C13	1.387 (7)
C4—H41	0.9900	C12—H12	0.9500
C4—H42	0.9900	C13—H13	0.9500
Se2—Se1—O1	164.75 (8)	H51—C5—H52	108.1
Se2—Se1—C2	88.74 (14)	O2—C6—C7	111.4 (4)
O1—Se1—C2	76.05 (16)	O2—C6—H61	109.3
Se1—Se2—C3	88.90 (15)	C7—C6—H61	109.3
C1—O1—Se1	104.8 (3)	O2—C6—H62	109.3

C5—O2—C6	111.2 (4)	C7—C6—H62	109.3
C2—N1—C1	114.8 (4)	H61—C6—H62	108.0
C3—N2—C2	120.6 (4)	N3—C7—C6	109.5 (4)
C3—N3—C4	124.1 (4)	N3—C7—H71	109.8
C3—N3—C7	122.3 (4)	C6—C7—H71	109.8
C4—N3—C7	113.5 (4)	N3—C7—H72	109.8
O1—C1—N1	124.3 (4)	C6—C7—H72	109.8
O1—C1—C8	119.8 (4)	H71—C7—H72	108.2
N1—C1—C8	115.9 (4)	C9—C8—C13	118.8 (4)
N1—C2—N2	120.1 (4)	C9—C8—C1	121.5 (4)
N1—C2—Se1	120.0 (3)	C13—C8—C1	119.6 (4)
N2—C2—Se1	119.9 (3)	C10—C9—C8	121.4 (5)
N2—C3—N3	119.1 (4)	C10—C9—H9	119.3
N2—C3—Se2	121.7 (3)	C8—C9—H9	119.3
N3—C3—Se2	119.2 (3)	C9—C10—C11	119.6 (5)
N3—C4—C5	110.5 (4)	C9—C10—H10	120.2
N3—C4—H41	109.5	C11—C10—H10	120.2
C5—C4—H41	109.5	C10—C11—C12	120.6 (5)
N3—C4—H42	109.5	C10—C11—H11	119.7
C5—C4—H42	109.5	C12—C11—H11	119.7
H41—C4—H42	108.1	C13—C12—C11	119.8 (5)
O2—C5—C4	110.9 (4)	C13—C12—H12	120.1
O2—C5—H51	109.5	C11—C12—H12	120.1
C4—C5—H51	109.5	C12—C13—C8	119.8 (5)
O2—C5—H52	109.5	C12—C13—H13	120.1
C4—C5—H52	109.5	C8—C13—H13	120.1

Se1—O1—C1—N1	−1.4 (5)	C6—O2—C5—C4	59.3 (6)
Se1—O1—C1—C8	178.9 (3)	N3—C4—C5—O2	−54.2 (6)
C2—N1—C1—O1	−0.3 (6)	C5—O2—C6—C7	−60.4 (6)
C2—N1—C1—C8	179.3 (4)	C3—N3—C7—C6	132.3 (5)
C1—N1—C2—N2	−177.3 (4)	C4—N3—C7—C6	−51.9 (5)
C1—N1—C2—Se1	2.5 (5)	O2—C6—C7—N3	55.4 (6)
C3—N2—C2—N1	178.4 (4)	O1—C1—C8—C9	−160.8 (4)
C3—N2—C2—Se1	−1.3 (5)	N1—C1—C8—C9	19.5 (6)
C2—N2—C3—N3	−177.1 (4)	O1—C1—C8—C13	18.0 (6)
C2—N2—C3—Se2	4.7 (6)	N1—C1—C8—C13	−161.7 (4)
C4—N3—C3—N2	−178.8 (4)	C13—C8—C9—C10	−1.4 (6)
C7—N3—C3—N2	−3.3 (7)	C1—C8—C9—C10	177.4 (4)
C4—N3—C3—Se2	−0.5 (6)	C8—C9—C10—C11	1.5 (7)
C7—N3—C3—Se2	174.9 (3)	C9—C10—C11—C12	−0.7 (7)
Se1—Se2—C3—N2	−4.6 (4)	C10—C11—C12—C13	−0.2 (7)
Se1—Se2—C3—N3	177.2 (4)	C11—C12—C13—C8	0.3 (7)
C3—N3—C4—C5	−132.6 (5)	C9—C8—C13—C12	0.5 (6)
C7—N3—C4—C5	51.6 (6)	C1—C8—C13—C12	−178.3 (4)